Evidence for Bound and Free Water Species in the Hydration Shell of an Aqueous Micelle

Sundaram Balasubramanian[a1*], Subrata Pal[b], and Biman Bagchi[b2*]

[a] Chemistry and Physics of Materials Unit,

Jawaharlal Nehru Centre for Advanced Scientific Research,

Jakkur, Bangalore 560064, India.

[b]Solid State and Structural Chemistry Unit, Indian Institute of Science,

Bangalore 560012, India.

Abstract

Our atomistic molecular dynamics simulations reveal the existence of bound and free water molecules in the hydration layer of an aqueous micelle. The bound water molecules can be either singly or doubly hydrogen bonded to the polar head group on the surface of the micelle. The ratio of bound to free water is found to be approximately equal to 9:1 at 300 K.

[1]email:bala@jncasr.ac.in

[2]email:bbagchi@sscu.iisc.ernet.in

1 Introduction

Water inevitably present at the surface of biological macromolecules and self-organized assemblies plays a critical role in the structure, stability and function of these systems [1, 2]. However, the layer of water that surrounds these systems is rather thin, typically 1-3 layers thick. Thus, the study of hydration layer has turned out to be rather difficult. Dielectric relaxation studies measure the collective response of the whole system and, therefore, are not a sensitive probe of the dynamics of the hydration water. NMR techniques (NOE and NMRD) have the required spatial resolution but lack the dynamic resolution. Neutron scattering techniques are beginning to be applied to study the dynamics of hydration layer in these systems [3]. Solvation dynamics may be a reasonably good probe because it can have both the temporal and spatial resolution [4, 5, 6], yet it provides only a collective response. In this circumstance, computer simulation can play a very important role in understanding the nature of the hydration water.

As the hydration layer is spatially heterogeneous even on a molecular length scale and because the microscopic interactions are quite complex, a purely analytical study of this system is prohibitively difficult. In order to capture some of the basic physics of the dynamics in such systems, a model in terms of a dynamic exchange between bound and free water molecules [7] has been proposed. The bound water molecules are those which are singly or doubly hydrogen bonded to the protein or to the surface of a self assembled aggregate while the free water molecules are not. The microscopic dynamical event is an exchange between these two states of water within the hydration layer. The model predicts the emergence of a slow decay when the binding energy is high. In this limit, the time constant of the slow decay is just the inverse of the rate of bound to free transition[7]. Although this model has been semi-quantitatively successful in explaining wide range of behavior, the basic assumption

of the existence of bound and free water molecules remained unsubstantiated.

In addition to the above, bound and free water molecules give a convenient way to categorize the water molecules in the hydration layer. The bound molecules can be further sub-divided into two categories – singly hydrogen bonded or doubly hydrogen bonded. We shall denote these two by IBW1 and IBW2, respectively. Free water molecules are denoted by IFW (interfacial free water).

Recently, we have presented several studies aimed at understanding various aspects of interfacial water [8]. These studies were based on detailed atomistic molecular dynamics (MD) simulations of an anionic micelle, CsPFO (Cesium pentafluorooctanoate). These studies have confirmed the existence of slow water and ion dynamics in the interfacial region. We have also studied the lifetime of hydrogen bonds that the water molecules form with the micellar polar head groups (PHG) and found that it becomes considerably longer than that between two water molecules in the bulk.

In the present work, we have extended our previous study to investigate in detail, the equilibrium structure of the interfacial water. Our study has clearly revealed (we believe for the first time) that the water at the interface of CsPFO consists of three different species – IBW2, IBW1 and IFW, in the ratio, 1.1:8:0.9, i.e., the bound to free water ratio is 9:1. This large ratio is a signature of the highly polar character of the anionic micelle.

2 Results

As the details of the simulation have been discussed elsewhere [8], we directly proceed to the discussion of the results. Figure 1 illustrates the average geometries adopted by IBW1 and IBW2 water species. The figure is not just an illustration – we have given all the details about average bond lengths and the bond angles *calculated* from

the simulation. There are features which are absent in IBW1 but present in IBW2, such as a well-defined distance between the water and the second (non-bonded) oxygen of the polar head group. This feature at 4.7Å is prominent for IBW2 water molecules but absent for IBW1. An examination of the full distribution of bond lengths and bond angles, and not just their averages, show that the environment around bound water species is, in general, more well defined relative a water molecule in pure water.

In figure 2 we present the monomer energy distribution, for all the three species, as also for water molecules in the bulk. It is seen that the interfacial water molecules have peaks at lower energies – the doubly bonded species (IBW2) have the lowest potential energy. It is also worth noting that the bound water molecules have considerably lower energy values than the the free water molecules. It is this enhanced stability which makes the bound species identifiable, even when they are transient because of the dynamic exchange between the free and bound species. A large part of this stabilisation comes from the stronger hydrogen bonds that bound water molecules form with the surfactant head groups.

In figure 3 we provide a schematic of the free energies of the three species, calculated from their average concentrations. Despite the reduced monomer energy arising out of two water-headgroup hydrogen bonds, the IBW2 state is less stable than the IBW1 state due to entropic considerations (less number of suitable configurations). The reversible reactions between these states of water on such a surface should determine the dynamical response of interfacial water.

Note that figure 3 describes the free energy and not the binding energy of the three species. The binding energy can be inferred from figure 2. The total binding energy of the IBW2 species is indeed larger than IBW1.

3 Conclusions

In conclusion we note that the existence of identifiable bound and free water molecules on the surface can indeed help in developing a phenomenological description of dynamics of water at complex interfaces. The 9:1 ratio obtained (for IBW and IFW) is expected to be typical for ionic micelles. However, this ratio is bound to decrease substantially for proteins due to the existence of hydrophobic and less polar amino acid groups in its surface. The water on the protein/membrane surface is expected to play a critical role in the molecular recognition of hydrophobic patches by incoming ligands or drug molecules. Work in this direction is under progress.

This work is supported by grants from the Department of Science and Technology and the Council of Scientific and Industrial Research, to both SB (JNC) and BB (IISC.).

References

[1] N. Nandi, K. Bhattacharyya, and B. Bagchi, Chem. Rev. **100**, 2013 (2000).

[2] D. Ringe, Curr. Op. Struct. Biol. **5**, 825 (1995); M.S.P. Sansom, I.H. Srivastava, K.M. Ranatunga, and G.R. Smith, Trends Biol. Sci. **25**, 368 (2000); M.M. Teeter, A. Yamano, B. Stec, and U. Mohanty, Proc. Natl. Acad. Sci. **98**, 11242 (2001); M. Tarek and D.J. Tobias, Phys. Rev. Lett. **88**, 138101 (2002); C. Mattos, Trends Biochem. Sci. **27**, 203 (2002); M. Marchi, F. Sterpone, and M. Ceccarelli, J. Am. Chem. Soc. **124**, 6787 (2002).

[3] S.V. Ruffle, I. Michalarias, J. Li, and R.C. Ford, J. Am. Chem. Soc. **124**, 565 (2002).

[4] N. Sarkar, A. Dutta, S. Das, and K. Bhattacharyya, J. Phys. Chem. **100**, 15483 (1996).

[5] X. J. Jordanides, M. J. Lang, X. Song, and G. R. Fleming, J. Phys. Chem. B **103**, 7995 (1999).

[6] R. E. Riter, D. M. Willard, and N.E. Levinger, J. Phys. Chem. B **102**, 2705 (1998).

[7] N. Nandi and B. Bagchi, J. Phys. Chem. B **101**, 10954 (1997).

[8] S. Balasubramanian and B. Bagchi, J. Phys. Chem. B **105**, 12529 (2001); S. Balasubramanian and B. Bagchi, J. Phys. Chem. B **106**, 3668 (2002); S. Pal, S. Balasubramanian, and B. Bagchi, J. Chem. Phys. **117**, 2852 (2002); S. Balasubramanian, S. Pal, and B. Bagchi, Curr. Sci. **82**, 845 (2002); S. Balasubramanian, S. Pal, and B. Bagchi, Phys. Rev. Lett. **89**, 115505 (2002).

FIGURE CAPTIONS

Fig. 1: Schematic description of the environment around bound interfacial waters, (a) IBW1, and (b) IBW2. Numerical values of the geometrical parameters are average values obtained from the MD run. Water molecules and surfactant headgroups are rigid entities in the interaction model. PHGO denotes the oxygen atom of the polar head group of the surfactant, and PHGC denotes the carbon atom in the head group. WO and WH denote the oxygen and hydrogen atoms of the interfacial water, respectively. The broken lines between PHGO and WH denote the hydrogen bond.

Fig. 2: Distribution of monomer energies of interfacial water molecules (solid lines) compared to that of bulk water (dashed line). Solid lines from right to left represent the data for IFW, IBW1, and IBW2 species, respectively.

Fig. 3: Schematic description of the free energy (solid line) and internal energy (dashed line) profiles of the interfacial water species. The species are in dynamical equilibrium with themselves and with water present in the bulk region of the micellar solution. The reaction coordinate is arbitrary and does not imply any distance. Barrier heights too are arbitrary.